The Korean Journal of Ceramics, 4 [4] 286 - 291 (1998)

Effect of Sintering Temperature on the Dielectric Property of Lead Magnesium Niobate-Lead Titanate Ceramics

Hak-In Hwang, Jong Man Jung* and Joon-Shik Park

Korea Electronics Technology Institute, Pyungtaek, Kyunggido 451-860, Korea
**Department of Physics, Dankook University, Cheonan, Choongnam 330-714, Korea*
(Received July 13, 1998)

Dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ceramics prepared by the columbite precursor method have been investigated as a function of the sintering temperature in the range of 1000~1250°C. The $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ceramics show typical relaxor ferroelectric behavior. As the sintering temperature increased, the dielectric constant increased and the phase transition temperature shifted to lower temperature. The TCK (temperature coefficient of dielectric constant) and VRK (variation rate of dielectric constant) increased with increasing sintering temperature. The $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ compositions sintered at 1250°C appear to be suitable for ferroelectric bolometer.

Key words : Dielectric property, Relaxor ferroelectric, $Pb(Mg_{1/3}Nb_{2/3})O_3$, $PbTiO_3$, TCK, Ferroelectric bolometer

I. Introduction

In 1958 Smolenskii and Agranovskaya[1] reported unusual dielectric properties in complex perovskites with the general formula $Pb(B_1B_2)$ where B_1 is a low valence cation (Mg^{+2}, Ni^{+2} and Fe^{+3}) and B_2 a high valence cation (Nb^{+5}, Ta^{+5} and W^{+6}). They observed anomalously large and broad dielectric maxima which shifted up in temperature with increasing frequency. Correspondingly, frequency dispersion in the dissipation factor was observed as well. Such characteristic features observed in the so-called relaxor ferroelectric compounds and their solid solutions have attracted special attention for electro strictive strain application,[2-4] electro-optic application[5,6] and ferroelectric bolometers.[6,7]

Among the relaxor ferroelectric materials, lead magnesium niobate ($Pb(Mg_{1/3}Nb_{2/3})O_3$-PMN) is the composition with an anomalously large dielectric constant and a broad diffuse transition temperature of -15°C at 1 kHz measuring frequency.[1] The structure of PMN is pseudo-cubic with space group Pm3m at room temperature,[8] with no evidence of long range ordering of the dissimilar B site cation in the ABO_3 perovskite structure.[9] This disorder in the B site cation is believed to be the basis of relaxor type behavior in such materials.[10] Though the transition temperature of PMN is well below room temperature, it can be easily shifted upward with $PbTiO_3$ (PT) additions, a 'normal' or ordered ferroelectric compound which has a transition at 490°C.[11,12]

The compositions of (1-x)PMN-xPT ($0.03 \leq x \leq 0.10$) are very candidate for electrical application because it shows high dielectric maximum, broad dielectric maximum around room temperature. In this study, we report the effect of sintering temperature on the dielectric properties of (1-x)PMN-xPT ($0.03 \leq x \leq 0.09$). The possibility for uncooled infrad-red radiation (IR) sensor application is mentioned.

The major IR sensor using ferroelectric material is pyroelectric IR sensor which is using the pyroelectric properties of ferroelectric material. Pyroelectric IR sensor used to obtain thermal image through wide temperature range, but it has disadvantages of lower peak detectivities and limited bandwidths of operation.[7] Ferroelectric bolometer, which is made by micromachining technology, shows low thermal mass and good thermal insulation.[13] When the external DC-bias field is applied to ferroelectric bolometer, the polarization near the transition temperature is stabilized, the dielectric constant depends mainly on temperature and the ferroelectric bolometer shows high responsivity of thermal image.[6,7] Therfore the linear variation vs. temperature behavior can be effective in ferroelectric bolometer. In this present paper, the dielectric properties of PMN-PT ceramics was investigated. The variation rate of dielectric constant (VRK) below transition temperature was studied.

II. Experimental Procedure

Polycrystalline ceramic samples across the (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$ were prepared by solid state reaction using the appropriate amount of reagent grade raw materials of PbO, MgO, Nb_2O_5 and TiO_2. Since it is well known that the formation of perovskite PMN is difficult to fabricate without the appearance of a parasitic pyrochlore phase ($Pb_3Nb_4O_{13}$), the columbite precursor method by Swartz and Shrout was used.[14] In the first stage a precursor columbite phase, $MgNb_2O_6$, was prepared by mixing MgO and Nb_2O_5 in stoichiometric ratio and calcined at

1000°C for 10 h. In the second stage, the precursor was mixed in stoichiometric ratios with PbO and TiO_2. An excess of 0.5 weight percent PbO was added to compensate for PbO volatility during calcining and sintering. The oxides were mixed using attrition milling in distilled water, dried and then calcined at 850°C for 4 h. The calcined powder was cold pressed to form disks followed by sintering from 1000°C to 1250°C for 2 hours in closed alumina crucibles. The sintered samples were characterized by X-ray diffraction (XRD). Microstructural variation of specimens was observed with scanning electron microscopy (SEM). The samples for electrical measurements were prepared from sintered pellets by polishing the faces with SiC grinding paper and electroding with silver paste. Temperature dependence of the dielectric constant and loss were measured at various frequencies (0.1 to 100 kHz) at a heating rate of 4°C/min by using an Impedance Analyzer (HP4192A). Prior to the electrical measurements each sample was poled by applying a DC field of 2 MV/m at -50°C for 30 min.

III. Results and Discussion

1. Sintering and X-ray analysis

Fig. 1 shows the microstructures of (1-x)PMN-xPT ceramics sintered from 1000°C to 1250°C for 2 h. There is remarkable difference in grain size and shapes for the compositions with varying sintering temperature. The SEM micrograph of the sample fired from 1000°C to 1150°C revealed a wide distribution of grain sizes and shapes with pores which were mostly located at the grain boundaries and grain junctions. Increasing the sintering temperature resulted grain growth. The ceramics sintered at 1250°C showed a dense microstructure with enlarged

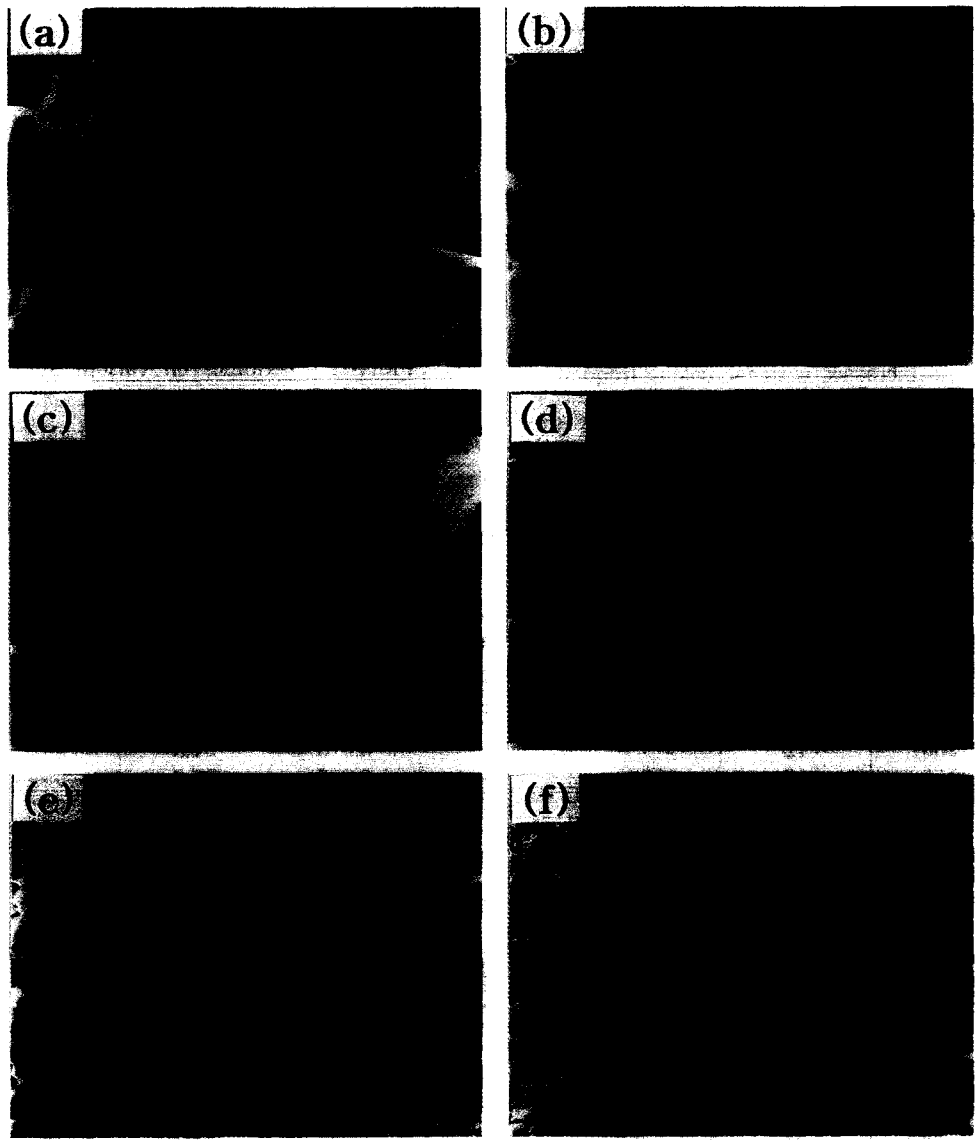

Fig. 1. SEM micrographs for the fracture surfaces of (1-x)PMN-xPT ceramics sintered from 1000°C to 1250°C for 2 h. (a) 1250°C (x=0.03), (b) 1250°C (x=0.07), (c) 1250°C (x=0.09), (d) 1150°C (x=0.09), (e) 1100°C (x=0.09) and (f) 1000°C (x=0.09).

grains which were substantially free pores. The grain size for the ceramics increased with an increase in sintering temperature and allowed rapid elimination of pores from the samples. A grain size variation of 1 to 10 μm can be seen for the ceramics sintered from 1000°C to 1250°C.

X-ray diffractometer was used to examine the formation of pyrochlore phase on the component surfaces. The relative amounts of the pyrochlore and perovskite phase were determined by measuring the X-ray peak intensities for the perovskite and pyrochlore phase [(110) and (222), respectively]. The percentage of perovskite phase was calculated using the following equation (1).

$$\text{Perov.}(\%) = \frac{I_{perov.}}{I_{perov.} + I_{pyro.}} \times 100 \quad (1)$$

For all compositions the amounts of perovskite phase is more than 88% for sintering temperature above 1000°C. The percentage of perovskite phase is summarized in Table 1. The variations in the density of (1-x)PMN-xPT ceramics with sintering temperature are shown in Table 1. As the sintering temperature increased, the density tended to increase and reached above 95% of the theoretical density above 1150°C.

2. Physical and dielectric properties

Fig. 2 shows the typical plot of the temperature dependence of dielectric constant (K) and dissipation factor (D) at various frequencies (0.1~100 kHz) for the composition 0.95PMN-0.05PT sintered at 1250°C for 2 h. The transition temperature increases with increasing frequency.

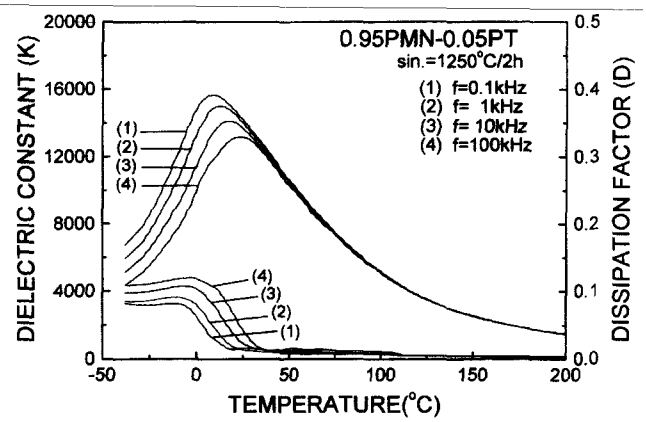

Fig. 2. Temperature dependence of dielectric constant and dissipation factor at various frequencies for 0.95PMN-0.05PT ceramic.

With increasing frequency the dielectric constant decreases in magnitude and the maxima shifts to higher temperature, while for the dissipation factor, the maxima increases with an increase in frequency. All of the compositions show a diffuse phase transition with a strong frequency dispersion. It is the characteristic of relaxor ferroelectric materials.

Fig. 3 shows the temperature dependence of the dielectric constant of the 0.95PMN-0.05PT system at 1 kHz sintered from 1000°C to 1250°C for 2 h. Fig. 4 shows the temperature dependence of the dielectric constant of the (1-x)PMN-xPT ceramic system at 1 kHz sintered at 1250°C for 2 h. The physical and dielectric properties of (1-x)PMN-xPT ceramics on various sintering temperature

Table 1. Dependence of the Physical and Electrical Properties of (1-x)PMN-xPT Ceramics on Various Sintering Temperatures

PMN-PT	Sintering Temp. (°C)	T_c (1 kHz) (°C)	K_{max} (1 kHz)	K (1 kHz) (25°C)	tanδ (1 kHz) (25°C)	Perov.%	Theo. Density (%)	Diffuseness (δ)
0.97-0.03	1250	-1	11438	9573	0.025	90.9	96.5	61
	1150	7	9286	8412	0.013	89.3	95.1	59
	1100	4	8694	10317	0.031	89.0	94.6	62
	1050	6	6341	5908	0.009	88.9	92.0	72
	1000	7	4070	3889	0.004	-	90.9	86
0.95-0.05	1250	12	15136	13975	0.013	91.3	96.9	45
	1150	17	10598	10374	0.017	90.3	95.7	59
	1100	18	8870	8691	0.013	89.6	93.7	60
	1050	18	6137	6056	0.025	90.5	92.9	68
	1000	19	5536	5488	0.007	90.8	90.8	76
0.93-0.07	1250	24	15211	15211	0.037	90.8	96.5	40
	1150	30	10053	9978	0.042	90.2	96.1	57
	1100	31	10091	10010	0.036	91.1	95.0	58
	1050	31	6617	6525	0.026	90.5	93.2	67
	1000	32	5114	5042	0.020	89.5	91.1	73
0.91-0.09	1250	35	20915	18505	0.014	92.4	96.7	38
	1150	40	10136	8832	0.046	88.9	95.7	55
	1100	42	8636	7575	0.053	90.9	92.6	58
	1050	42	7140	6405	0.034	92.3	93.4	63
	1000	42	5932	5425	0.027	-	91.1	68

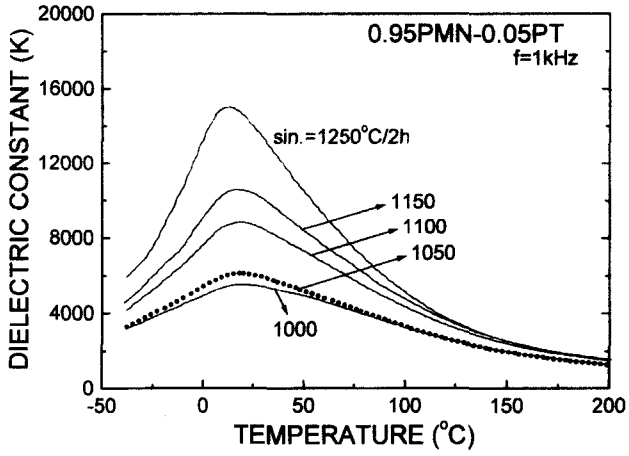

Fig. 3. Temperature dependence of dielectric constant of 0.95PMN-0.05PT ceramic sintered from 1000°C to 1250°C for 2 h.

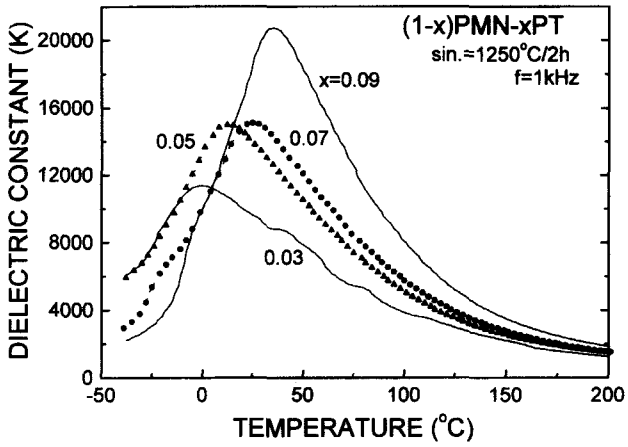

Fig. 4. Temperature dependence of dielectric constant of (1-x)PMN-xPT ceramics sintered at 1250°C for 2 h (x=0.03-0.09).

are presented in Table 1.

The solid solution appeared to cause a slight shift in phase transition temperature (T_C) to lower temperature with increasing sintering temperature up to 1250°C. The dielectric constants were found to improve with increasing sintering temperature. The dielectric constant increased with increasing grain size. Thus the increase in dielectric constant with increasing grain size is ascribed to the decrease in amount of grain boundaries which contained the pyrochlore, impurities *et al.* which are deterious to the dielectric constant. The corresponding dissipation factor values decreased with increasing sintering temperature.

Fig. 5 shows variation in transition temperature with composition x of system (1-x)PMN-xPT series with varing sintering temperature. The phase transition temperature is continuously shifted to higher temperature with increase of small amounts of PT, their rates of increase are about 6°C/mol% for all the compositions. And the phase transition temperature appeared to cause a slight shift to lower

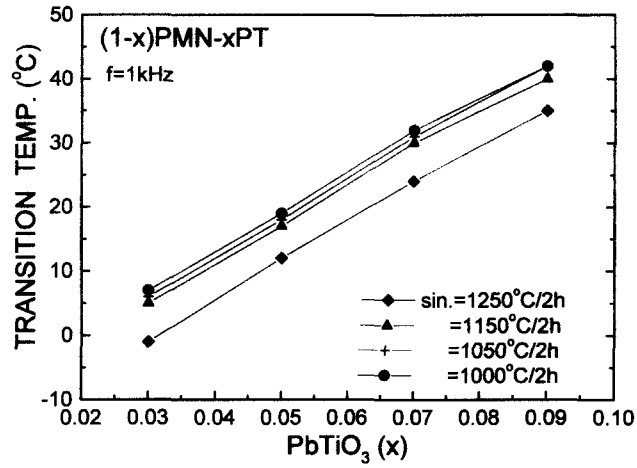

Fig. 5. Variation of phase transition temperature of (1-x) PMN-xPT ceramics for various sintering temperature.

temperature with increasing temperature up to 1250°C.

There is growing need for ceramic materials for ferroelectric bolometer with high dielectric constant, high temperature dependence of dielectric constant and phase transition temperature around room temperature.[13] And the materials which have low firing temperature have been valued highly because it allows the use of low-cost electrode. Ferroelectric bolometer under DC-bias field shows stabilized polarization and the dielectric constant depends mainly on temperature.[7] Therefore, the linear VRK characteristic below transition temperature can be effective factor in ferroelectric bolometer. In order to investigate the dielectric behavor below transition temperature, we examined the temperature coefficient of dielectric constant (TCK) and VRK characteristics defined as equations (2) and (3).

$$TCK(\%) = \frac{K_T - K_{25℃}}{K_{25℃}} \times 100 \quad (2)$$

$$VRK = \frac{\Delta K}{\Delta T} \qquad (T < T_c) \quad (3)$$

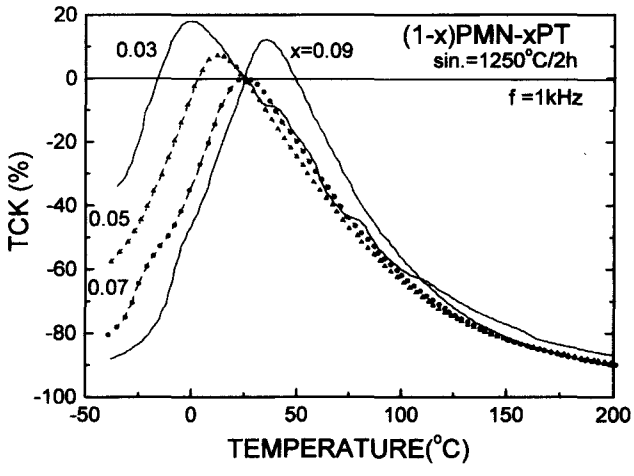

Fig. 6. TCK vs. temperature behavior for (1-x)PMN-xPT ceramics sintered at 1250°C for 2 h.

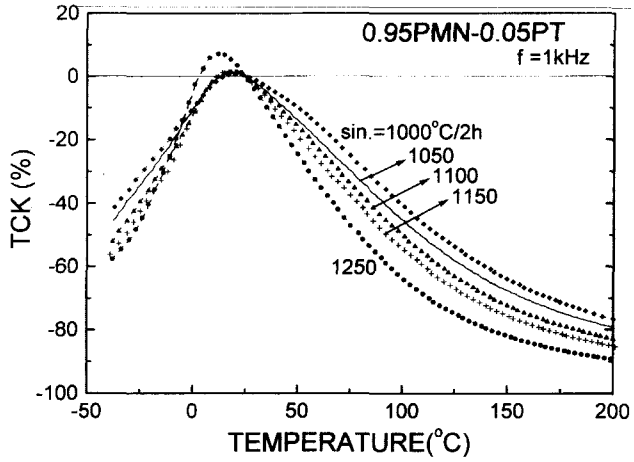

Fig. 7. TCK vs. temperature behavior for 0.95PMN-0.05PT ceramics for various sintering temperature.

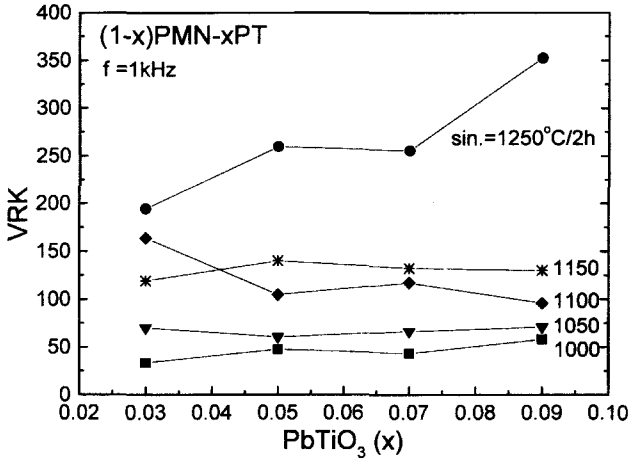

Fig. 8. VRK vs. PT mole fraction behavior for (1-x)PMN-xPT ceramics with varying sintering temperaure.

Fig. 6 shows the temperature dependence of TCK for the compositions (1-x)PMN-xPT sintered at 1250°C for 2 h. At below phase transition temperature, (1-x)PMN-xPT series show almost linear TCK characteristic. Fig. 7 shows the TCK for the composition 0.95PMN-0.05PT with varing sintering temperature. The TCK characteristic vs. temperature increased with increasing sintering temperature. The composition 0.91PMN-0.09PT sintered at 1250°C for 2 h shows a T_c of 35°C, tanδ~1.4% at room temperature and good TCK characteristic. However, these compositions sintered at 1250°C which is higher than the melting point of Ag used as electrode material for application. Further work is in progress to evaluation the dielectric properties of the system by using low sintering agents.

Fig. 8 shows the VRK characteristic for the composition (1-x)PMN-xPT with varying sintering temperature. The VRK increased as the firing temperature increased. The samples fired from 1000°C to 1150°C showed similar VRK value unrelated with PT mole fraction. For the sample sintered at 1250°C, the VRK increased as the mole fraction of PT increased. This means that high VRK can be achieved by increasing sintering temperature.

The ceramic samples fired at 1250°C show dense microstructure, linear TCK and high VRK characteristics. This property means that they can be used for ferroelectric bolometer which is apply for thermal imaging, fire-services, security surveillance and industrial process control.

IV. Conclusions

(1-x)PMN-xPT ceramics show a diffuse phase transition with a strong frequency dispersion. And the phase transition temperature (T_c) appeared to cause a slight shift to lower temperature with increasing sintering temperature up to 1250°C. The dielectric constant and dissipation factor were found to improve with increasing sintering temperature.

The TCK and VRK characteristic increased with increasing sintering temperature. At below phase transition temperature, the (1-x)PMN-xPT ceramics show almost linear TCK characteristics. The high VRK can be obtained when the sample was fired at 1250°C. The VRK increased with increasing PT mole fraction when the sample was fired at 1250°C.

The (1-x)PMN-xPT ceramics sample fired at 1250°C show dense microstructure, linear TCK and high VRK characteristics which is suitable for ferroelectric bolometer.

References

1. G. A. Smolenskii and A. I. Agranovskaya, "Dielectric Polarization of a Number of Complex Compounds," *Sov. Phys.: Solid State*, **3**(10), 1429-1437 (1959).
2. K. Uchino, S. Nomura, L. E. Cross, S. J. Jang and R. E. Newnham, "Electrostrictive Effects in Lead Magnesium Niobate Single Crystals," *J. Appl. Phys.*, **51**(2), 1142-1145 (1980).
3. S. L. Swartz, T. R. Shrout, W. A. Schulze and L. E. Cross, "Dielectric Properties of Lead Magnesium Niobate Ceramics," *J. Am. Ceram. Soc.*, **67**(5), 311-314 (1984).
4. T. R. Shrout, U. Kumar, M. Megherhi, N. Yang and S. J. Jang, "Grain Size Dependence of Dielectric and Electrostriction of $Pb(Mg_{1/3}Nb_{2/3})O_3$-based Ceramics," *Ferroelectrics*, **76**, 479-487 (1987).
5. W. A. Bonner, E. F. Dearborn, J. E. Geusic, H. M. Marcos and U. I. Letert, "Dielectric and Electro-optical Properties of Lead Magnesium Niobate," *Appl. Phys. Lett.*, **10**(5), 163-165 (1967).
6. R. W. Whatmore, P. C. Osbond and N. M. Shorrocks, "Ferroelectric Materials for Thermal IR Detectors," *Ferroelectrics*, **76**, 351-367 (1987).
7. R. W. Whatmore, A. Patel, N. M. Shorrocks and F. W. Ainger, "Ferroelectric Materials for Thermal IR Sensors State-of-the-art and Perspectives," *Ferroelectrics*, **104**, 269-283 (1990).
8. V. A. Bokov and I. E. Myl'nikova, "Electrical and Optical

Properties of Single Crystals of Ferroelectrics with Diffuse Phase Transition," *Sov. Phys.: Solid State*, **3**(3), 613-623 (1961).
9. G. A. Smolenskii, V. A. Isupov, A. I. Agranovskaya and S. N. Popov., "Ferroelectrics with Diffuse Phase Transitions," *Sov. Phys.: Solid State*, **2**, 2584-2594 (1961).
10. I. W. Chen, P. Li and Y. Wang, "Structure Origin of Relaxor Perovskites," *J. Phys. Chem. Solids*, **57**(10), 1525-1536 (1996).
11. S. W. Choi, T. R. Shrout, S. J. Jang and A. S. Bhalla, "Morphotropic Phase Boundary in $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ System," *Mater. Lett.*, **8**(6,7), 253-255 (1989).
12. S. W. Choi, J. M. Jung and A. S. Bhalla, "Morphotropic Phase Boundary in Relaxor Ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ Ststem," *Ferroelectrics*, **189**, 27-38 (1996).
13. Y. S. Lee, "Uncooled IR Detector," *Phys. High Tech.*, **7**(2), 22-26 (1998).
14. S. L. Swartz and T. R. Shrout, "Fabrication of Perovskite Lead Magnesium Niobate," *Mater. Res. Bull.*, **17**, 1245-1250 (1982).